



Structural and optical properties of ZnSe quantum dots in glass nanocomposites



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HIGHLIGHTS

- ZnSe quantum dots embedded glass-nanocomposites were synthesized.
- Nanocrystal sizes were controlled by the heat treatment schedule.
- Structure and optical properties of nano-sized ZnSe in glass were investigated.
- Strong visible red photoluminescence was obtained from these nanocomposites.

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ABSTRACT

Zinc selenide (ZnSe) quantum dots (QDs) were synthesized in a dielectric (borosilicate glass) matrix for the first time by melt-quenching process followed by thermal treatment. Sizes of the quantum dots were varied by post thermal treatment. UV–Vis optical absorption spectroscopy, transmission electron microscopy (TEM) and Raman spectroscopy were deployed to investigate the ZnSe QDs. TEM analysis reveals QD sizes of the order of 2–4 nm and relatively larger nanocrystals having sizes of the order of 15–26 nm. The sizes of the QDs have also been verified with the help of effective mass approximation model and optical absorption spectroscopy. The quantum confinement effect has been observed for both variation of heat treatment temperature and time. The Raman spectra of the nanocomposites reveal blue-shifted Raman peaks of ZnSe at 295 and 315 cm^{−1} due to phonon confinement effect. The decrease in Raman intensity with heat treatment indicates increase in size of the QDs. Red luminescence from the ZnSe-glass nanocomposites peaking at 708 nm due to the size related as well as traps related states makes their applications towards luminescent solar concentrators (LSCs).

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1. Introduction

Nanostructured materials exhibit interesting novel properties that are surprisingly different from their bulk properties. The sizes of the nanomaterials offer the opportunity to control these properties, mainly their optical properties. Particularly, the II–VI semiconductors (ZnS, ZnSe, CdS, CdSe, etc.) show maximum response to the size related properties within 1–100 nm size range. Semiconductor nanocrystals (NCs) having sizes comparable to the exciton Bohr radius shows three dimensional quantum confinement effect. These semiconductor NCs having such small

dimensions are called the quantum dots (QDs). These QDs modify the optical properties like optical absorption, photoluminescence (PL) and the nonlinear refractive index towards the application field of optical communication and optical limiters [1,2]. Again their wide band gap values, high quantum efficiency and availability in multiple colors (based on their sizes) make themselves as a replacement to the traditional phosphors in many areas such as solid-state lighting devices, luminescent materials, and biological applications [3,4]. So, the optical properties of these II–VI semiconductor nanoparticles have been the most investigated topic in this recent decade apart from their other usages in memory element devices [5] and applications towards second harmonic generations [6].

Zinc selenide (ZnSe) is the less investigated material compared to the other II–VI compound semiconductors such as ZnS, CdS,

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CdSe, etc. even though it is an important semiconductor material with a wide band gap (~2.70 eV). High-performance blue/ultraviolet-light-sensitive ZnSe-nanobelts have been investigated and details can be found in published literature [7]. ZnSe has been used in II–VI light-emitting diodes (LEDs) and diode lasers working in the blue-light region as they are much sensitive to UV/blue light. Synthesis of ZnSe NCs in glass matrix and their luminescence at two photon absorption, second harmonic generation has been reported in the literature [8]. Colloidal ZnSe NCs having PL in the spectral range 390–440 nm has also been investigated [9]. Photoelectric properties of ZnSe nanostructures have also been reported by Philipose et al. [10].

Multiple physical and chemical methods have been used to synthesize II–VI semiconductor nanostructures. Some physical process such as molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) approaches are taken to form quantum dots [11,12] and vapor–liquid–solid (VLS) approaches to form quantum wires [13,14]. Besides these, synthesis of semiconductor NCs in glass matrix by sol–gel process has also been reported [15]. But the report on the synthesis of II–VI semiconductor NCs by the melt-quenching technique followed by thermal treatment is very few [16–18]. Again in the maximum cases, the commercial filter glasses have been taken as the precursor glasses for the study [19,20]. So the synthesis and optical properties of ZnSe QDs embedded glass nanocomposites are particularly appealing.

In this paper, we report the synthesis of ZnSe QDs by a single step in-situ process in $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--Na}_2\text{O--K}_2\text{O--B}_2\text{O}_3$ system. The sizes of the NCs were controlled by varying the thermal treatment temperature and time. The optical properties were examined by studying the optical absorption spectra, Raman spectra and size of these NCs were estimated using the effective mass approximation model. The PL properties of the ZnSe nanostructured dielectric nanocomposites are also discussed.

2. Experimental

2.1. Preparation of dielectric nanocomposites

In this work, ZnSe NCs are synthesized in a glass system with nominal composition of $49\text{SiO}_2\text{--}3\text{Al}_2\text{O}_3\text{--}4\text{Na}_2\text{O--}31\text{K}_2\text{O--}13\text{B}_2\text{O}_3$ (wt. %) and 0.6 wt.% ZnSe was added to the base glass. Quartz, SiO_2 (Bremthaler/Quarzitwerk, Usingen, Germany), alumina, Al_2O_3 (99%; Aldrich, Milwaukee, Wisconsin), sodium carbonate, Na_2CO_3 (Anhydrous GR, Loba Chemie, India) potassium carbonate, K_2CO_3 (Anhydrous GR, Loba Chemie, India), boric acid, H_3BO_3 (99.5%; Fluka Chemika, GmbH, Buchs, Germany) and zinc selenide, ZnSe (Powder, 99.99%, Aldrich, Germany) were utilized as raw materials for the formation of the glass. In the first step of the synthesis, the powder mixtures of the raw materials was prepared and melted at 1500°C for 1.5 h in an alumina crucible. Then the melt was quickly cooled to room temperature by pouring it into a preheated iron mould. Then the as quenched glass was annealed at 450°C for 1 h to remove the residual thermal stress. In the second step, the samples were sized from the as prepared glass and then thermally treated at different temperatures and times. Then the thermally treated samples were grinded and polished before performing the absorption and PL experiments.

2.2. Characterization

The glass transition temperature (T_g), the deformation temperature (T_d) and the coefficient of linear thermal expansion (CTE) were measured using a horizontal push rod dilatometer (DIL 402 PC, Netzsch). Density of the glass samples was determined using

density measurement accessories supplied with a Mettler Toledo balance by Archimedes method. Here water was employed as the buoyancy liquid. TEM studies were carried out using a Tecnai G2 30ST (FEI Company) operating at an accelerating voltage of 300 kV. Raman spectra were recorded by using micro Raman spectrometer (Renishaw InVia Reflex) with excitation of argon ion (785 nm) laser. The laser power was fixed at sufficiently low value to circumvent heating effect of the samples and spectra were collected with a resolution of 1 cm^{-1} . The UV–Vis absorption spectra and the UV–Vis PL spectra of the polished 2 mm thick samples were also recorded using fiber optic spectrometer (AvaSpec-3648-USB2, Avantes) and a diode laser source of wavelength 446 nm.

3. Results and discussion

3.1. Density and thermal properties

The 0.6 wt.% ZnSe added precursor glass sample is designated as ZS-0h. The glass transition temperature (T_g), dilatometric deformation temperature (T_d) and the coefficient of thermal expansion (CTE) of ZS-0h were determined by using a dilatometer. The value of T_g and T_d were found to be 527°C and 559°C . CTE was determined over the temperature range $50\text{--}400^\circ\text{C}$ and found to be $12.2 \times 10^{-6}\text{ K}^{-1}$. The ZnSe added precursor glass was heat treated at 530, 540 and 550°C for a constant duration (10 h) and are assigned as ZS-530C-10h, ZS-540C-10h and ZS-550C-10h. Then the precursor glass was thermally treated at 550°C for several durations (from 10 h to 50 h) and their details including sample identifications are given in Table 1. The densities of those samples have also been measured and the values are listed in Table 1.

3.2. Absorption spectra

The optical absorption spectra of the precursor and all thermally treated ZnSe-glass nanocomposites in the UV–Visible region have been taken at room temperature. Fig. 1 represents the optical absorption spectra of the samples subjected to different thermal treatment temperatures at a fixed duration of 10 h. The absorption spectra of the base glass have also been shown in the figure for comparison. Three absorption peaks (~370, 500 and 780 nm) have been obtained from this spectra. The first two peaks around 370 and 500 nm are due to ZnSe NCs of two different sizes [21]. The first peak (~370 nm) corresponds to strongly confined ZnSe NCs or quantum dots and second peak (~500 nm) is associated with bulk like NCs of ZnSe. The absorption peak around 365–395 nm for ZnSe was reported by Li et al. [22] and Reiss et al. [9]. The formation and growth of ZnSe NCs have also been evidenced from the absorption spectra. The absorbance value of the nanocomposites increases with the increase in heat treatment temperature indicating formation of more ZnSe NCs. Two peaks which appeared around 370 nm and 500 nm are slightly red shifted validating formation of small amount of larger NCs from smaller NCs, though the increase in NC size is small (Table 1). Choi and his co-workers [23,24] argued that Se^{2-} color centers also show similar absorption band when silicate glasses are prepared with ZnSe. It is also reported that the optical absorption band around 500 nm is attributed to Se^{2-} [25]. The possibility of presence of Se^{2-} color centers in the glass-nanocomposites has been discussed in the TEM and Raman spectroscopy section.

In case of any direct band gap semiconductor subjected to electrical dipole allowed transition, the relation between absorbance and incident photon energy is given by the Eq. (1).

$$\alpha(h\nu) = C^* \left(h\nu - E_g^{\text{bulk}} \right)^{\frac{1}{2}} \quad (1)$$

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